

Application Data Sheet

No.97

GC-MS

Gas Chromatograph Mass Spectrometer

Procedures for Creating MRM Methods for Multicomponent Simultaneous Analyses Using Retention Indices

To create MRM analysis methods, it is necessary to configure the analysis time program based on the retention times for the target compounds. However, when creating multicomponent simultaneous analysis methods for more than 100 components, considerable time and effort is needed to analyze all the standards, and calculate the retention times.

The GCMSsolution control software (ver. 4.20 and later) for the GCMS-TQ series is equipped with a Smart MRM method creation function. Smart MRM is linked to the AART (Automatic Adjustment of Retention Time) function, and calculates retention times for the measured components from just a single n-alkane analysis. In addition, an analysis time program is configured automatically based on the calculated retention times. This Data Sheet introduces the procedures for creating these MRM methods for multicomponent simultaneous analysis.

1. Preparing the Smart Database File Containing the Retention Indices

Begin by preparing the Smart Database, the database file in which the target compound transitions and retention indices are registered.

The Smart Pesticides Database is pre-registered with transitions and retention indices for approximately 480 pesticide components. It allows the user to create MRM analysis methods without performing the method development to determine transitions, collision energies, and retention indices.

In addition, users can also create a Smart Database themselves. Using the MRM Optimization Tool, the optimum transitions and collision energies can be found automatically, thus making it possible to create the database file easily. For details, refer to Application Data Sheet No. 98.

Note: If a user already has a quantitative method file for MRM mode, the existing method file data can be used as is in the Smart Database file by importing it into Smart Database.

Compound Name (E)	Ion1				Ion2				Ion3			
	Type	m/z	CE	Ratic	Type	m/z	CE	Ratic	Type	m/z	CE	Ratic
Aldicarb deg.	T	115.1>100.1	8	100.00	Ref.1	115.1>68.0	8	104.06	Ref.2	115.1>48.0	12	40.47
DCP	T	121.1>45.0	4	100.00	Ref.1	121.1>77.0	8	48.09	Ref.2	121.1>49.0	24	11.56
Azinylcarb deg.	T	80.0>46.0	6	100.00	Ref.1	80.0>50.0	4	3.94	Ref.2	80.0>48.0	28	9.73
Chlorfentozine deg.	T	137.0>102.0	14	100.00	Ref.1	137.0>75.0	26	37.61	Ref.2	137.0>61.0	26	19.58
Thymoxazol	T	99.0>71.0	8	100.00	Ref.1	99.0>54.0	26	6.13				
Methamidophos	T	141.0>95.0	8	100.00	Ref.1	141.0>126.0	4	18.74	Ref.2	141.0>79.0	22	31.28
Dichlorvos	T	185.0>93.0	14	100.00	Ref.1	185.0>109.0	14	28.66	Ref.2	185.0>63.0	22	25.82
Nitenzoxin	T	149.1>71.1	8	100.00	Ref.1	149.1>102.1	6	67.94	Ref.2	149.1>84.1	4	18.82
Azinphos	T	138.1>96.0	6	100.00	Ref.1	138.1>110.1	6	53.98	Ref.2	138.1>81.0	6	42.47
Dicofenoxin	T	170.0>100.0	24	100.00	Ref.1	170.0>136.0	14	101.98	Ref.2	170.0>110.0	14	10.99
EPTC	T	189.1>128.1	4	100.00	Ref.1	189.1>86.0	12	22.96	Ref.2	189.1>160.1	8	10.85

Fig. 1: Smart Pesticides Database

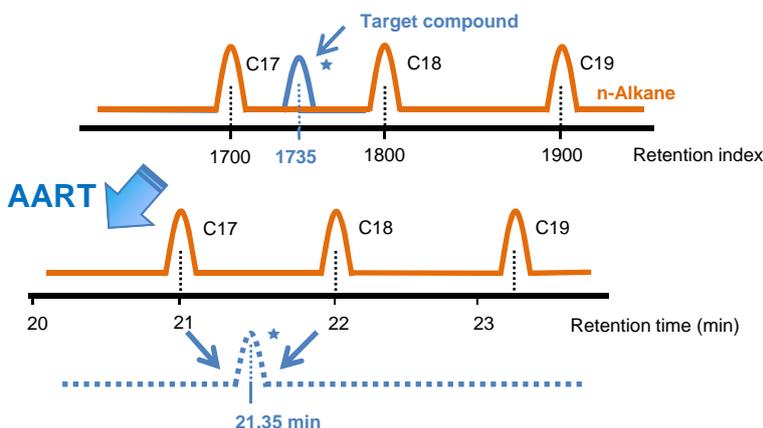
2. Measuring the Mixed Standard n-Alkane Solution

Next, measure the standard n-alkane solution to correct the retention times registered in Smart Database. Correct the retention times for the registered target compounds based on the n-alkane identification results.

AART (Automatic Adjustment of Retention Time) Function

Retention Index values are relative to the retention times for the target compounds and the retention time for n-alkane. If the retention time for n-alkane is known, then the retention time for a target compound can be calculated based on the Retention Index. This is referred to as the AART function. The AART function provides multipoint correction using retention times for multiple alkanes differing in carbon number. As a result, the retention times for compounds with a wide range of boiling points can be calculated with high accuracy.

Using the AART function, target compound retention times can be calculated without analyzing standard samples for the target compounds.



*If you need exact retention time, please analyze the standard sample.

3. Creating MRM Analysis Methods Using the Smart MRM Method Creation Function

Step (i) Run the GCMS Postrun program. Display the n-alkane data file.
Check that the n-alkane peaks are identified correctly.

Step (ii) Click  to display the Smart MRM window.

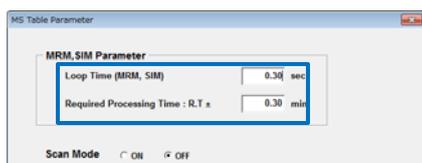
Step (iii) Select the target compounds and transitions.

Type	Acq. Mode	Method No.	Compound Name (E)	Ion1				Ion2				Ion3			
				Type	m/z	CE	Ratio	Type	m/z	CE	Ratio	Type	m/z	CE	Ratio
Target	MRM	1	Aldicarb deg.	T	115.1>100.1	8	100.00	Ref.1	115.1>88.0	8	104.06	Ref.2	115.1>48.0	12	40.47
Target	MRM	1	DCBP	T	121.1>40.0	4	100.00	Ref.1	121.1>77.0	8	48.09	Ref.2	121.1>49.0	24	11.96
Target	MRM	1	Aldicarb deg.	T	80.0>95.0	6	100.00	Ref.1	80.0>50.0	4	3.91	Ref.2	80.0>48.0	28	9.73
Target	MRM	1	Chlorfenvinphos deg.	T	137.0>102.0	14	100.00	Ref.1	137.0>75.0	26	37.61	Ref.2	137.0>51.0	26	19.36
Target	MRM	1	Hymexazol	T	99.0>71.0	8	100.00	Ref.1	99.0>54.0	26	6.13				
Target	MRM	1	Methamidophos	T	141.0>95.0	8	100.00	Ref.1	141.0>126.0	4	18.71	Ref.2	141.0>79.0	22	31.28
Target	MRM	1	Dichlorvos	T	185.0>93.0	14	100.00	Ref.1	185.0>109.0	14	26.66	Ref.2	185.0>63.0	22	25.82
Target	MRM	1	Neresistoxin	T	149.1>71.1	8	100.00	Ref.1	149.1>102.1	6	67.94	Ref.2	149.1>84.1	4	18.52
Target	MRM	1	Allidochlor	T	138.1>96.0	6	100.00	Ref.1	138.1>110.1	6	63.98	Ref.2	138.1>81.0	6	62.47
Target	MRM	1	Dichlorbifenil	T	170.9>100.0	24	100.00	Ref.1	170.9>136.0	14	101.98	Ref.2	170.9>110.0	14	10.99

Selection of target compounds

Selection of transitions for quantification and identification

Step (iv) Set the MRM parameters.

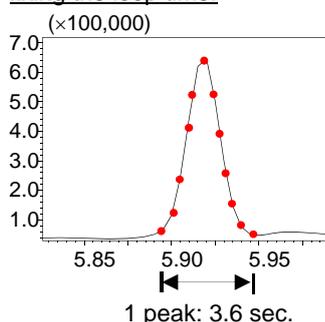


(1) Retention Time
The compound retention times are acquired based on the n-alkane data displayed in step (i).

(2) Loop Time
This is the sum of the event times for all compounds configured in one group. For example, if this is set to 0.3 seconds, data on each compound will be acquired every 0.3 seconds.

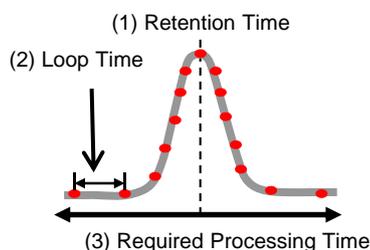
(3) Required Processing Time
This shows the measurement time range, centered on the corrected retention time. For example, if this is set to 0.3 minutes, compound data will be acquired for the retention time ±0.3 minutes.

Peaks with good repeatability can be obtained by fixing the loop time.

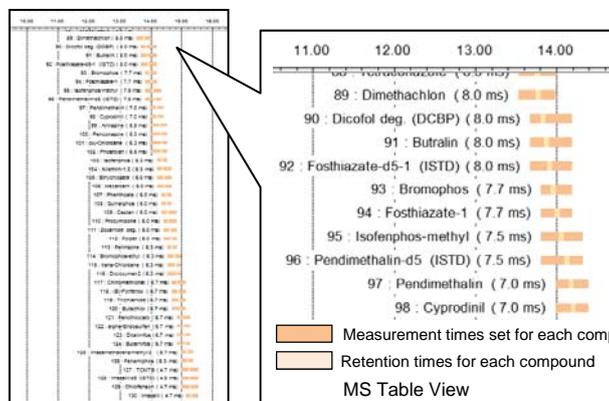


The loop time has an impact on repeatability. At least 10 data points must be collected to ensure a peak with good repeatability¹⁾. For example, as shown in the figure at left, if the width of a peak is 3.6 seconds, then fixing the loop time at 0.3 seconds enables the collection of peaks with good reliability.

If the loop time is set to 0.3 seconds, then 12 data points are collected.



Step (v) Check the measurement time range for each compound.



The measurement time range for each compound can be checked in the MS table view window. MRM analysis methods created using Smart MRM are configured with the optimal measurement times for each component. Data is only collected for the elution time for the target components. As a result, multiple components can be analyzed simultaneously without compromising sensitivity, even in multicomponent simultaneous analyses.

420 pesticide components were simultaneously analyzed using an MRM analysis method created with Smart MRM. The results are introduced in Application Data Sheet No. 96. With the optimal MRM analysis method created by Smart MRM, favorable sensitivity and accuracy were obtained even in a simultaneous analysis of 420 components.

4. Summary

By using Smart MRM, it was possible to create an MRM method for simultaneous analysis without analyzing analytical standards for the target compounds. With MRM analysis methods created by Smart MRM, data are only acquired for the elution time for the target components. As a result, simultaneous analysis even for multiple components can be performed without compromising sensitivity.

References

1) J. Sep. Sci 25 (2002) 608 J. Dalluge et al